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14. ABSTRACT
The symposium "Tutorials in Nanotechnology: Focus on Physical and Analytical Electrochemistry" was held at the 216th Meeting of the Electrochemical Society in Vienna Austria on the 5th of October 2009. This symposium was part of a continuing series of symposia at Electrochemical Society meetings that present and educate the audience on the use and application of nanotechnology in electrochemical research. These tutorials cover the fundamental physical chemistry of nanotechnology, along with the application and incorporation of nanotechnology into electrochemical systems as well as the employment of electrochemistry as a tool for the characterization of nanomaterials. Nanotechnology has played a revolutionary role in physical and analytical electrochemistry over the last decade, and the present symposium sought to highlight this impact by bringing together six world renowned scientists to present their ground breaking research involving nanotechnology in physical and analytical electrochemistry. The symposium presentations were very well received by those present, and the attendance was a standing room only audience of well over 200.

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Final Report - Tutorials in Nanotechnology: Focus on Physical and Analytical Electrochemistry

Principal Investigator: Paul C. Trulove
Organization: The Electrochemical Society, Pennington NJ 08534-2839

I. Abstract

The symposium "Tutorials in Nanotechnology: Focus on Physical and Analytical Electrochemistry" was held at the 216th Meeting of the Electrochemical Society in Vienna Austria on the 5th of October 2009. This symposium was part of a continuing series of symposia at Electrochemical Society meetings that present and educate the audience on the use and application of nanotechnology in electrochemical research. These tutorials cover the fundamental physical chemistry of nanotechnology, along with the application and incorporation of nanotechnology into electrochemical systems as well as the employment of electrochemistry as a tool for the characterization of nanomaterials. Nanotechnology has played a revolutionary role in physical and analytical electrochemistry over the last decade, and the present symposium sought to highlight this impact by bringing together six world renowned scientists to present their ground breaking research involving nanotechnology in physical and analytical electrochemistry. The symposium presentations were very well received by those present, and the attendance was a standing room only audience of well over 200.

II. Summary of the Symposium

The symposium was held at the 216th Meeting of the Electrochemical Society. This was the most attended meeting in Electrochemical Society history with over 3500 international participants and more than 3000 technical papers presented in numerous symposia. The guiding philosophy for these symposia, including the Tutorials in Nanotechnology, is based on the stated objectives of The Electrochemical Society that are

- *To advance the theory and practice of electrochemistry, solid state sciences, and allied subjects;*
- *To encourage the research and dissemination of knowledge in these fields; and*
- *To promote the education of fundamental and applied scientists and engineers in these fields.*

Tutorials in Nanotechnology: Focus on Physical and Analytical Electrochemistry represented the fourth addition of this important symposium series. The goal of these symposia is to both to inform and educate scientists and engineers who are not practitioners in the area of nanotechnology. The symposium presentations are by invitation only. Organizers enlist a select group of leading researchers in the field of nanotechnology to present their latest research in the context of the larger field. The hoped for result of these symposia is to broaden the participation of scientists and engineers in nanotechnology research.

Each version of this symposium has a specific research focus within the broad area of nanotechnology. The current version was focused on Physical and Analytical Chemistry in the context of nanotechnology. Below are some of the topics that were covered by the speakers at this symposium.

- *Synthesis, Characterization and Electrochemical Application of Nanopores*
- *Electroanalytical Methods in Nanotechnolgy*
- *Electrochemical Methods for the Synthesis and Characterization of Nanomaterials*
- *Electrochemistry at the Nanoscale*
- *Applications of Scanning Probe Microscopy to the study of Electrochemistry at the Nanoscale*
- *Physical Electrochemistry at the Nanoscale*

Each of these topics is important to the application of electrochemistry to nanotechnology, and they are also areas that have significant impact on topics of interest to the Air Force Office of Scientific Research and the DoD as a whole (e.g., chemical and biological sensing, advanced materials, compact power, and advanced computing). The organizers assembled an impressive group of world leading investigators involved in the application of Physical and Analytical Chemistry to nanotechnology. A list of these speakers and the titles of their presentations are given in Appendix II and the abstracts for these presentations are given in Appendix III. The presentations given by these invited speakers provided the audience with an unequalled opportunity to sample the state-of-the-art in Physical and Analytical Chemistry at the nanoscale, and hopefully this has, in turn, helped stimulate expanded research into this important area.

Appendix I: Call for Papers

Tutorials in Nanotechnology: Focus on Physical and Analytical Electrochemistry - An Invited Symposium

(All Divisions)

Nanotechnology has played a revolutionary role in physical and analytical electrochemistry over the last decade. These tutorials will cover the fundamental physical chemistry of nanotechnology, along with the application and incorporation of nanotechnology into electrochemical systems as well as the employment of electrochemistry as a tool for the characterization of nanomaterials. These tutorials are expected to cover both theories of nanotech systems as well as synthetic production of these materials.

Appendix II: Invited Speakers and Presentations

Tutorials in Nanotechnology: Focus on Physical and Analytical Electrochemistry

Monday October 5, 2009

Carl Wagner Memorial Award Presentation: Electrochemistry in Synthetic and Biological Nanopores

A. Schibel, T. Edwards, R. Kawano, W. Lan, D. Holden and **H. S. White** (University of Utah)

Nanoscience, Nanotechnology, and Analytical Methods: A Selective Tutorial

M. Ratner (Northwestern University)

Application of Electrochemical and Electrogenerated Luminescence Methods to Studies of Metallic and Semiconductor Nanoparticles

A. Bard (University of Texas)

Electrochemistry at the Nanoscale: Building Blocks and Techniques

H. Abruna (Cornell University)

Into the Nanoscale with Scanning Electrochemical Microscopy?

W. Schuhmann (Ruhr-Universität Bochum)

Tutorials in Nanotechnology: Focus on Physical and Analytical Electrochemistry

H. Wolfschmidt, T. Brulle, O. Paschos (Technische Universita et Muenchen) and **U. Stimming** (Technische Universität München)

Appendix III: Presentation Abstracts

Electrochemistry in Synthetic and Biological Nanopores

Anna E.P. Schibel, Thomas Edwards, Ryuji Kawano,
Wenjie Lan, Deric Holden, and Henry S. White
Department of Chemistry
University of Utah
SLC, UT 84112

This presentation will described recent investigations of molecular and particle transport in synthetic nanopores and protein ion channels. Our research has focused on the use of nanopores for single molecule detection, particle analysis, and sequencing of biopolymers (e.g., DNA) using glass and quartz nanopore membranes. A method is described for fabricating 25 to 75 µm-thick fused quartz membranes containing a single conical shaped nanopore (orifice radius ranging from 10 to 1000 nm). The quartz nanopore membrane (QNM) provides an excellent solid support structure for lipid bilayers in ion channel recordings due to the large electrical resistivity of fused quartz. Electrical measurements demonstrate that the leakage current through 1,2-diphytanoyl-*sn*-glycero-3-phosphocholine (DPhPC) bilayers suspended across the orifice of ~900 nm-radius QNMs is immeasurably small, corresponding to bilayer resistances greater than 10^{12} ohms. The QNMs were used to observe the translocation of single-stranded DNA oligimers (poly-dA 50-mer and poly-dA 20-mer) through the ion channel α-hemolysin reconstituted in a DPhPC bilayer suspended across the QNM orifice. Detection and counting of 28-nm-radius polystyrene nanoparticles using a 50-nm radius orifice QNM are also demonstrated. Nanoparticle detection events through the QNM were simulated using finite element software.

Nanoscience, Nanotechnology, and Analytical Methods: A Selective Tutorial

Mark Ratner
Department of Chemistry and Department of
Materials Science and Engineering
Northwestern University
Evanston, Illinois
60208 USA

Because nanostructures have much larger surface to volume ratios than do macroscopic samples of any material, the significance of surface chemistry and surface phenomena is accentuated in such structures. Historically, this was certainly recognized by Faraday, and was the basis for some of his important early experiments on what we now call nanotechnology. Most properties of nanostructures follow from this dominance of surface phenomena. The tutorial will focus on two topics: first, the area of analytical electrochemistry, including sensing modalities using nanodots. Here we will focus on locality and amplification, on electrochemical sensing of biotargets, and on competitive sensing modes along with aspects of identification and practicality. One interesting challenge is the transition from cartoons through calculations to understanding. The second topic will be physical electrochemistry: transport through molecular bridges and adlayers. Here the focus will be first on injection into, out of, and through single molecules between two electrodes, and molecular layers between electrodes. We will discuss some aspects of crowding in the molecular environment, and of electrostatics. Finally, there will be a discussion of inelastic behaviors for obtaining understanding both of geometries and of possible transport pathways using observations of inelastic transport. Some specific examples will be given, and methods for attaining understandings in this area will be stressed.

Application of Electrochemical and Electrogenerated Luminescence (ECL) Methods to Studies of Metallic and Semiconductor Nanoparticles

Allen J. Bard
The University of Texas at Austin
Department of Chemistry and Biochemistry
Austin, Texas 78712

Many nanoparticles (NPs) of metals and semiconductors have been synthesized in recent years and have been characterized by a number of methods, such as transmission electron microscopy and various spectroscopic techniques. Interest in this area can be attributed to both fundamental aspects, e.g. understanding the behavior of nm-size particles in contrast to the bulk material, and in possible applications of NPs, e.g. as catalysts or analytical labels. Compared with spectroscopic methods, there have been relatively few electrochemical studies. Many of these have looked at electron transfer behavior of the particles themselves dispersed in solution or as thin films. These have shown, for example, novel stepwise electron transfer reactions, e.g. of gold particles by Murray and others, and of semiconductor particles, like Si and CdSe. In addition, electrogenerated chemiluminescence (ECL) of semiconductor NPs has been seen. The basics of this field will be reviewed and new experiments involving electrochemistry of more complex NP structures, e.g. core/shell and mixtures of NPs, and of studies of collisions of single nanoparticles with an ultramicroelectrode, will be discussed. Studies of single nanoparticles at an inert electrode provide a new approach to the characterization of single particle properties and could form the basis of highly sensitive analytical techniques.

Electrochemistry at the Nanoscale: Building Blocks and Techniques

Hector Abruna
Cornell University
Chemistry and Chemical Biology
Baker Lab.
Ithaca, New York 14853-1301

This presentation will focus on the synthesis and characterization via electrochemical, STM and transport measurements of molecular assemblies, of deliberate design, for application in molecular devices. We have prepared and characterized single-molecule devices incorporating transition metal complexes and fullerens designed so that electron transport occurs through welldefined charge states of a single molecule. We have also employed more complex molecular architectures. Preliminary results with novel optical techniques and new device geometries including mechanical break junctions will also be discussed.

Into the nanoscale with scanning electrochemical microscopy?

Wolfgang Schuhmann
Analytische Chemie - Elektroanalytik & Sensorik,
Ruhr-Universität Bochum, Universitätsstr. 150,
D-44780 Bochum; Germany

Scanning electrochemical microscopy (SECM) has emerged to a versatile tool for visualization of chemical activities at liquid/solid and liquid/liquid interfaces. Additionally, SECM was successfully applied for electrochemically induced microstructuring. The tutorial lecture will introduce into the basic principles of high-resolution SECM highlighting:

1) Specific features of SECM instrumentation for highresolution SECM imaging
2) Fabrication of nanoelectrodes and positioning of nanoelectrodes in SECM
3) Constant-distance positioning as a prerequisite for the application of nanoelectrodes in SECM
4) Integration of electrodes within AFM cantilevers
5) Applications of high-resolution SECM in materials and biological research

Tutorials in Nanotechnology: Focus on Physical and Analytical Electrochemistry

Holger Wolfschmidt[1], Tine Brülle[1], Odysseas Paschos[1]
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Emerging advances in nanotechnology may offer new capabilities for enhancing the efficiency of electrochemical devices such as fuel cells and electrolyzers. Recent advances in energy research show that nanostructuring surfaces with a rational design of metallic catalysts can enhance their electrocatalytic activity. Even though there are a few examples that demonstrate the technology for designing and synthesizing selective nanocatalysts in some chemical reactions, a deliberate design has not been significantly advanced yet. Major challenges in nanotechnology applied to electrochemistry are the understanding of electrochemical phenomena and manipulating electrochemically active sites at the nanometer scale. The application of nanotechnology in energy research would accelerate the development of new materials (e.g. electrodes and electrolytes) as well as improve the overall design of the systems and components.

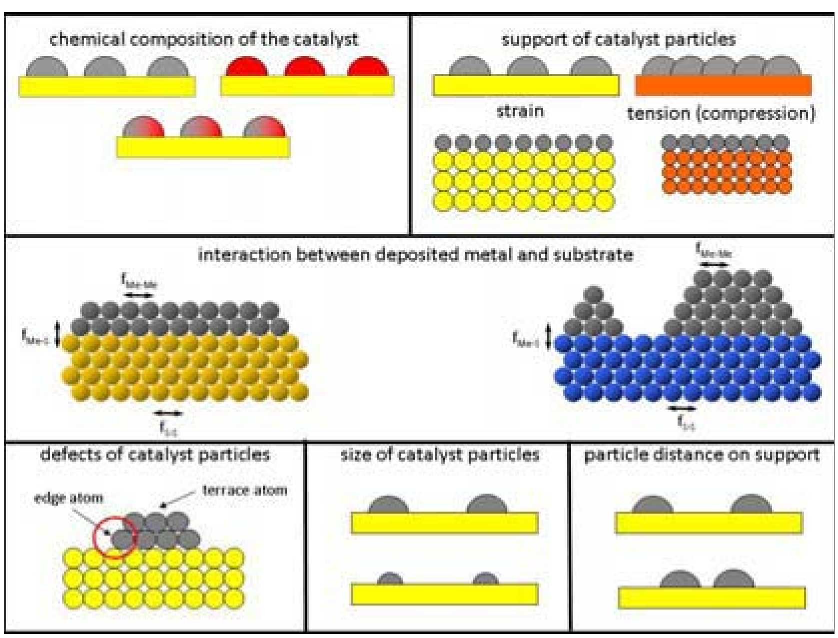

Fig.1: Parameters that can affect the electrochemical activity of catalysts

Previous work performed in our group shows that nanostructuring surfaces with electrochemically active materials (e.g. Pt and Pd) can improve their performance towards hydrogen related reactions, such as hydrogen evolution (HER) and hydrogen oxidation (HOR) reactions, with simultaneously decreasing the amount of precious metal catalyst used. Pd decorated Au(111) surfaces showed that by decreasing the Pd amount on Au(111), an increase of the activity for hydrogen evolution reaction (HER) occurred for small coverages[1]. A similar trend was observed for the case of Pt nanostructured Au(111) surfaces[2] but for even smaller coverages of Pt. It was reported that a possible explanation of this increase could be attributed to an effect of the substrate material. Hammer et al.[3] and Eikerling et al.[4] showed that the choice of substrate material can affect the performance of the catalyst system by the so-called strain and spill-over effects. However the choice of substrate material is only one parameter. There are other parameters such as the morphology of the catalyst particles (e.g. particle size, particle height, inter-particle distance) and the choice of catalyst material.

In order to get a deeper understanding of how different parameters affect the electrocatalytic activity, hydrogen related reactions such as HER and HOR were investigated on three different catalyst systems. These systems are all based on Pt as the catalyst material and Au(111), Cu and highly oriented pyrolytic graphite (HOPG) as the substrate materials. The influence of different parameters on the above mentioned reactions (HOR and HER) is investigated by using electrochemical methods (e.g. potentiostatic pulse techniques). The morphological and structural properties of the model catalysts is studied by electrochemical atomic force microscopy (EC-AFM) and scanning tunneling microscopy (EC-STM). Therefore, we can develop pathways to optimize the design and suggest catalyst structures that will have the potential for a high and efficient electrocatalytic activity.

An overview over various techniques of preparation, the analysis of structures and their catalytic activities will be given.

1. S. Pandelov and U. Stimming, *Electrochim. Acta* **52**, 5548 (2007)
2. H. Wolfschmidt, R. Bussar and U. Stimming, *J. Phys.Condens. Matter* **20**, 374127 (2008)
3. B. Hammer and J. K. Norskov, *Advances in Catalysis* **45,** 71 (2000)
4. M. Eikerling, J. Meier and U. Stimming, *Zeitschrift für Physikalische Chemie – International Journal of Research in Physical Chemistry & Chemical Physics*, **217**, 395 (2003)